Inorg. Chem. **1996,** *35,* 991−994 **991**

Volume Profile for Substitution in Labile Chromium(III) Complexes: Reactions of Aqueous $[Cr(Hedta)OH_2]$ and $[Cr(edta)]^-$ with Thiocyanate Ion

Colin L. Beswick, Richard D. Shalders, and Thomas W. Swaddle*

Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada T2N 1N4

Received August 24, 1995[⊗]

A procedure is given for correcting optical absorbance measurements made at variable pressure with a le Noble−Schlott (“pillbox”) cell for the inner sleeve wall thickness. With this technique, the molar volume change for the acid ionization of aqueous $[Cr(Hedta)OH_2]$ was found to be $+5.1 \pm 0.6$ cm^3 mol^{-1} (0−200 MPa, 25.0 °C, ionic strength 1.0 mol L^{-1} $HClO_4/NaClO_4$), an anomalous positive value which implies a change from quinquedentate to predominantly sexidentate edta and expulsion of the coordinated water on ionization. For thiocyanate substitution into labile $[Cr(Hedta)OH_2]$, high pressure stopped-flow measurements gave the volume of activation as -7.8 ± 0.9 cm^3 mol^{-1} and the volume of reaction as $+3 \pm 2$ cm^3 mol^{-1}, while for the reaction of $[Cr(edta)]^-$ with NCS^- the activation volume is -13.6 ± 0.6 cm^3 mol^{-1} (same conditions). These and other data support the notion that the anomalous substitutional lability of Cr^{III}(edta) complexes relative to typical Cr^{III} species is due to activation by transient chelation of the pendant arm of quinquedentate edta.

Although substitution at chromium(III) centers is normally slow (time scale of hours or days),[1] there exist at least three types of Cr^{III} complexes that are substitutionally labile (stopped-flow regime): porphyrin complexes,[2−4] Schiff-base chelates,[5,6] and complexes with the potentially sexidentate ligand edta and related species.[7−13] It has been reasonably concluded[1b,2−4] that lability in chromium(III) porphyrin complexes arises from electronic factors that favor a simple dissociatively activated (D or I_d) pathway. The mechanisms of labilization in the Schiff-base and edta complexes are less obvious. The lability of $[Cr(salen)(OH_2)_2]^+$ and related Schiff-base complexes[7] has been attributed to a destabilizing distortion of the ground state,[5] but this distortion has been described as slight.[14] The high reactivity of Cr^{III} complexes of edta, on the other hand, is thought to derive from the fact that the edta ligand in, e.g., $[Cr(Hedta)OH_2]$ is quinquedentate rather than sexidentate in acidic aqueous solution[15] and may facilitate the departure of the leaving group by transient coordination of the carboxyl group of the pendant arm.[8−12] The picture is complicated, however, by the likelihood[16−19] that edta is predominantly sexidentate in its complex with Cr^{III} in the pH range 3.5−6.5, i.e., that the conjugate base of $[Cr(Hedta)OH_2]$, which we will designate for the time being as “$[Cr(edta)OH_2]^-$”, is actually present mainly as $[Cr(edta)]^-$.

We have therefore sought further mechanistic information on Cr^{III} lability from the effects of pressure on the kinetics and equilibria of the reactions of thiocyanate ion with the edta and salen complexes of Cr^{III} in acidic aqueous solution. Unfortunately, in our hands, all attempts at stopped-flow kinetic measurements on the $[Cr(salen)(OH_2)_2]^+−NCS^-$ reaction were foiled by the prompt precipitation of the uncharged product $[Cr(salen)(OH_2)NCS]$, even when the published procedures of Rajendra Prasad et al.[5] were closely followed. We encountered no such problems with the corresponding reaction of the Cr^{III} edta complex, but in acidic aqueous solution this exists as a mixture of $[HLCrOH_2]$ and, nominally, $[LCrOH_2]^-$ ($L = edta^{4-}$), and, furthermore, complexation by NCS^- is incomplete; consequently, the pressure dependences of the acid ionization constant K_a of $[HLCrOH_2]$ (pK_a 1.75 at 25 °C and 0.1 MPa, ionic strength $I = 1.0$ mol L^{-1} [20]) as well as of both the forward and reverse rate constants of the two concurrent substitution reactions had to be determined (eq 1).

$$\begin{tikzcd}
\text{"}[LCrOH_2]^{-}\text{"} + H^+ + NCS^- \arrow[r, shift left, "k_1"] \arrow[d, shift left] & {[LCrNCS]^{2-} + H^+ + H_2O} \arrow[l, shift left, "k_{-1}"] \arrow[d, shift left] \\
{[HLCrOH_2] + NCS^-} \arrow[r, shift left, "k_2"] \arrow[u, shift left, "K_a"'] & {[HLCrNCS]^- + H_2O} \arrow[l, shift left, "k_{-2}"] \arrow[u, shift left, "K_a^{CrNCS}"']
\end{tikzcd} \qquad (1)$$

For simplicity, the kinetic measurements were made in strongly acidic solutions ($[H^+] = 0.10−0.44$ mol L^{-1}) in which

---

* Corresponding author. E-mail: swaddle@acs.ucalgary.ca. Telephone: (403) 220-5358. Fax: (403) 289-9488.

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1996.

(1) Swaddle, T. W.: (a) *Coord. Chem. Rev.* **1974**, *14*, 217; (b) *Adv. Inorg. Bioinorg. Mech.* **1983**, *2*, 95.

(2) Fleischer, E. B.; Krishnamurthy, M. *J. Am. Chem. Soc.* **1971**, *93*, 3784.

(3) Ashley, K. R.; Leipoldt, J. G.; Joshi, V. K. *Inorg. Chem.* **1980**, *19*, 1608.

(4) O’Brien, P.; Sweigart, D. A. *Inorg. Chem.* **1982**, *21*, 2094.

(5) Rajendra Prasad, D.; Ramasami, T.; Ramaswamy, D.; Santappa, M. *Inorg. Chem.* **1980**, *19*, 3181; **1982**, *21*, 850.

(6) Lloret, F.; Julve, M.; Mollar, M.; Castro, I.; Latorre, J.; Faus, J.; Solans, X.; Morgenstern-Badarau, I. *J. Chem. Soc. Dalton Trans.* **1989**, 729.

(7) $edta^{4-}$ = ethylenedinitrilo-*N,N,N′,N′*-tetraacetate, $(^-O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2^-)_2$; $salen^{2-}$ = *N,N′*-ethylenebis(salicylideneaminate), $^-OC_6H_4CH{=}NCH_2CH_2N{=}CHC_6H_4O^-$.

(8) Sulfab, Y.; Taylor, R. S.; Sykes, A. G. *Inorg. Chem.* **1976**, *15*, 2388.

(9) Ogino, H.; Watanabe, T.; Tanaka, N. *Chem. Lett.* **1974**, 91; *Inorg. Chem.* **1975**, *14*, 2093.

(10) Ogino, H.; Shimura, M.; Tanaka, N. *Inorg. Chem.* **1979**, *18*, 2497.

(11) Ogino, H.; Shimura, M. *Adv. Inorg. Bioinorg. Mech.* **1986**, *4*, 107.

(12) Ogino, H.; Masuko, A.; Ito, S.; Miura, N.; Shimura, M. *Inorg. Chem.* **1986**, *25*, 708.

(13) Guardalabene, J.; Gulnac, S.; Keder, N.; Shepherd, R. E. *Inorg. Chem.* **1979**, *18*, 22.

(14) Coggon, P.; McPhail, A. T.; Mabbs, F. E.; Richards, A.; Thornley, A. S. *J. Chem. Soc. A* **1970**, 3296.

(15) Thorneley, R. N. F.; Sykes, A. G. *J. Chem. Soc., Chem. Commun.* **1968**, 340.

(16) Wheeler, W. D.; Legg, J. I. *Inorg. Chem.* **1984**, *23*, 3978.

(17) Kaizaki, S.; Mizu-uchi, H. *Inorg. Chem.* **1986,** *25*, 2732.

(18) Kanamori, K.; Kawai, K. *Inorg. Chem.* **1986**, *25*, 3711.

(19) Yoshitani, K. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2115.

(20) In this article, concentrations refer to 21 °C and 0.1 MPa; adjustment for other temperatures and pressures when calculating equilibrium or rate constants is neither necessary nor desirable (see: Hamann, S.; le Noble, W. J. *J. Chem. Educ.* **1984**, *61*, 658).

0020-1669/96/1335-0991$12.00/0

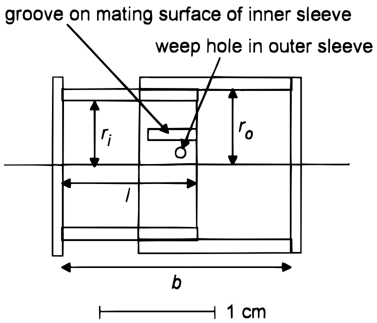

Figure 1. Le Noble−Schlott cell. Dimensions: $r_o = 0.77$ cm; $r_i = 0.64$ cm; $l = 1.15$ cm; b is variable.

the thiocyanato product is, in effect, exclusively $[HLCrNCS]^-$ ($pK_a^{CrNCS} = 3.39^{10}$). Thus, the pressure dependence of the rate constant k_{-1} for the aquation of $[LCrNCS]^{2-}$ was not directly measurable; nor was it practical to determine k_{-1} indirectly by measuring the pressure dependences of the overall rate constant k_{-1}' for aquation of $[HLCrNCS]^-$ to "$[LCrOH_2]^-$" ($k_{-1}' = k_{-1}K_a^{CrNCS}$) and of K_a^{CrNCS} by independent spectrophotometry, since too many pressure-dependent variables were involved in the latter. Fortunately, the key mechanistic information sought in this study can be extracted quite satisfactorily from data obtained at high acid concentrations.

Experimental Section

The purple solid $[Cr(Hedta)OH_2]$ was made by the method of Hamm[21] and was recrystallized twice from water. Its optical spectrum in 0.10 mol L^{-1} $HClO_4$ ($I = 1.00$ mol L^{-1}, $NaClO_4$) showed absorbance maxima at 387 and 545 nm. The effect of pressure on this spectrum as a function of pH was determined on a Cary Model 5E spectrophotometer with optical fiber cables leading to an Aminco 41-11551 high pressure optical vessel, maintained at 25.0 °C with a jacket through which water was circulated from an external thermostat. Inside the pressure vessel, the solution sample was contained in a le Noble−Schlott "pillbox" cell[22] (Hellma Canada Ltd., Concord, Ontario; Figure 1). The pressurizing fluid was distilled water, which was isolated from the hydraulic oil from the handpump and pressure intensifier by a free-piston separator. Pressures were measured on the sample side of the separator with a Heise Bourdon gauge, calibrated against a Pressurements T3800/4 deadweight gauge. Solution absorbances so measured at atmospheric pressure were converted to apparent molar absorbances ϵ by calibration against absorbances of the same solutions measured with conventional cuvettes in the Cary 5E.

Kinetic measurements were made at 0.1−200 MPa using a Hi-Tech HPSF-56 high pressure stopped-flow spectrophotometer set at 510 nm and thermostated at 25.0 ± 0.2 °C. Pressures were measured with an Autoclave Engineers digital gauge, calibrated as above. After mixing, $[Cr]_{total}$ was 3.04 mmol L^{-1}, I was 1.00 mol L^{-1} ($HClO_4/NaClO_4/NaNCS$), and $[NCS^-]$ was 0.0500−0.300 mol L^{-1}, to within 0.3% at worst. The absorbance changes were analyzed on a dedicated Apple IIe computer using Hi-Tech software, and followed first-order kinetics precisely (correlation coefficient better than 0.9995), typically giving first-order rate constants k_{obsd} with standard errors ±0.1%.

Results

Pressure Dependence of K_a. The le Noble−Schlott cell is designed[22] to collapse longitudinally under pressure as the contents compress, so that if the wall of the inner cylinder were of negligible thickness, there would be no purely volumetric effect on the measured absorbance. In practice, a small correction for the wall thickness needs to be applied for precise work. If the measured absorbances at atmospheric ("zero") pressure and pressure P are A_0 and A_P, the corresponding apparent molar absorbances are ϵ_0 and ϵ_P, and the specific volumes of the solvent are V_0 and V_P, respectively, then, designating the cell dimensions as in Figure 1, we have

Table 1. Pressure Dependences of the Molar Absorbances of $[Cr(Hedta)OH_2]$ and "$[Cr(edta)OH_2]^-$" and the Acid Dissociation Constant of $[Cr(Hedta)OH_2]$[a]

P/MPa	ϵ_H/L mol^{-1} cm^{-1} [b]	ϵ_A/L mol^{-1} cm^{-1} [b]	$K_a/10^{-2}$ mol L^{-1}
0.1	137.3 ± 1.2	197.0 ± 1.5	1.69 ± 0.31
6.0	136.9 ± 1.5	196.4 ± 1.8	1.87 ± 0.43
40.7	136.9 ± 1.1	196.7 ± 1.4	1.68 ± 0.29
80.3	137.3 ± 1.1	195.4 ± 1.6	1.44 ± 0.27
120.4	137.7 ± 0.9	195.6 ± 1.3	1.36 ± 0.20
159.7	137.5 ± 1.4	194.2 ± 2.1	1.26 ± 0.30
200.7	137.6 ± 1.3	193.3 ± 2.1	1.21 ± 0.29

[a] 25.0 °C, $I = 1.0$ ($HClO_4/NaClO_4$). [b] 545 nm.

$$\epsilon_P = \epsilon_0 b_0 (A_P/A_0)[\{(b_0 - l) + (r_i^2/r_o^2)l\} + (V_0/V_P)\{1 - (r_o^2/r_i^2)\}l] \quad (2)$$

where b_0 is the optical path length b measured at zero pressure.

Values of ϵ_P for solutions made up from $[Cr(Hedta)OH_2]$ (3.0×10^{-3} mol L^{-1}) in $HClO_4/NaClO_4$ ($I = 1.0$ mol L^{-1}) were measured at 25.0 °C over the pressure range 0.1−200 MPa at $[H^+]$ ranging from 9.33×10^{-5} to 0.934 mol L^{-1}, and were corrected according to eq 2 using V_0/V_P values for water from Schmidt and Grigull.[23] At a particular wavelength (545 nm) and pressure P, the equilibrium constant K_a for the acid ionization of $[HLCrOH_2]$ was calculated, along with the respective molar absorbances ϵ_H and ϵ_A for $[HLCrOH_2]$ and "$[LCrOH_2]^-$", by nonlinear least-squares fitting of the measured apparent molar absorbance ϵ_P to eq 3. The results are collected

$$\epsilon_P = \epsilon_A + \{(\epsilon_H - \epsilon_A)[H^+]/(K_a + [H^+])\} \quad (3)$$

in Table 1, in which it is seen that ϵ_H is independent of pressure (average: 137.3 ± 0.3 L mol^{-1} cm^{-1}) because 545 nm is an absorbance maximum for $[HLCrOH_2]$. Values of ln K_a were found to be a linear function of P within the experimental uncertainty

$$\ln K_a = \ln K_a^0 - (\Delta V_a/RT)P \quad (4)$$

which implies that the volume of acid ionization ΔV_a of $[HLCrOH_2]$ is independent of pressure over the range 0−200 MPa. This gives $K_a^0 = (1.77 \pm 0.05) \times 10^{-2}$ mol L^{-1} and $\Delta V_a = +5.1 \pm 0.6$ cm^3 mol^{-1}, at 25.0 °C and $I = 1.0$ mol L^{-1}.

Pressure Dependence of Rate Constants. At a given pressure and acid concentration, the observed rate constants k_{obsd} were linear functions of $[NCS^-]$, within the experimental uncertainty

$$k_{obsd} = k_b + k_f[NCS^-] \quad (5)$$

where k_f and k_b are the conditional rate constants for the formation and aquation, respectively, of $[HLCrNCS]^-$ from the mixture of "$[LCrOH_2]^-$" and $[HLCrOH_2]$. Values of k_f and k_b obtained by linear least-squares regression are collected in Table 2. The respective individual formation rate constants k_1^0 and k_2^0 for zero pressure (cf. eq 1) and the corresponding volumes of activation $\Delta V_1^‡$ and $\Delta V_2^‡$ were calculated by fitting all the k_f data simultaneously to the combined equations 4, 6, 7, and 8 (cf. Ogino et al.[10]), incorporating the values of K_a^0 and ΔV_a

---

[21] Hamm, R. E. *J. Am. Chem. Soc.* **1953**, *75*, 5670.
[22] le Noble, W. J.; Schlott, R. *Rev. Sci. Instrum.* **1976**, *47*, 770.
[23] Schmidt, E.; Grigull, U. *Properties of Water and Steam in SI Units*, 2nd ed.; Springer: New York, 1981.

Table 2. Rate Constants for the Formation (k_f) and Aquation (k_b) of $[Cr(Hedta)NCS]^-$ in Acidic Aqueous Solution[a]

$[H^+]$/mol L^{-1}	P/MPa	k_f/L mol^{-1} s^{-1}	k_b/s^{-1}
0.439	0	1.466	0.0589
	40	1.704	0.0744
	80	1.963	0.0854
	120	2.24	0.1024
	160	2.43	0.1335
	200	2.95	0.1411
0.316	0	1.510	0.0838
	40	1.826	0.0985
	80	2.09	0.1139
	120	2.41	0.1391
	160	2.73	0.1638
	200	3.03	0.210
0.211	0	1.998	0.0919
	40	2.24	0.1189
	80	2.52	0.1524
	120	2.95	0.1762
	160	3.38	0.207
	200	3.89	0.249
0.1007	0	2.86	0.1431
	40	3.321	0.1836
	80	3.73	0.245
	120	4.30	0.287
	160	5.12	0.339
	200	5.82	0.417

[a] Equation 5; 25.0 °C, $I = 1.0$ mol L^{-1} ($NaClO_4/HClO_4/NaNCS$).

obtained as described above.

$$k_f = (k_1K_a + k_2[H^+])/(K_a + [H^+]) \qquad (6)$$

$$k_1 = k_1^0 \exp(-P\Delta V_1^{\ddagger}/RT) \qquad (7)$$

$$k_2 = k_2^0 \exp(-P\Delta V_2^{\ddagger}/RT) \qquad (8)$$

For k_b, the equation corresponding to eq 6 is[10]

$$k_b = (k_{-1}K_a^{CrNCS} + k_{-2}[H^+])/(K_a^{CrNCS} + [H^+]) \qquad (9)$$

but, since $K_a^{CrNCS} \approx 4 \times 10^{-4}$ mol L^{-1} [10] $\ll [H^+]$ in our experiments, eq 9 can be reduced to

$$k_b = (k_{-1}K_a^{CrNCS}/[H^+]) + k_{-2} = (k_{-1}'/[H^+]) + k_{-2} \qquad (10)$$

$$k_{-1}' = k_{-1}'^0 \exp(-P\Delta V_{-1}'^{\ddagger}/RT) \qquad (11)$$

$$k_{-2} = k_{-2}^0 \exp(-P\Delta V_{-2}^{\ddagger}/RT) \qquad (12)$$

where $\Delta V_{-1}'^{\ddagger} = \Delta V_{-1}^{\ddagger} + \Delta V_a^{CrNCS}$. At any given pressure, k_b was indeed found to be linearly dependent on $[H^+]^{-1}$, and the ln k_{-1}' and ln k_{-2} values so obtained were linear functions of P. For consistency with the treatment of the data for the formation reactions, however, the k_b values were fitted globally to the combined equations 10−12. Table 3 summarizes the results. The zero-pressure rate and equilibrium constants are in good agreement with those of Ogino et al.[10]

Discussion

The unequivocally *positive* volume change ΔV_a (= +5.1 ± 0.6 cm^3 mol^{-1} at $I = 1.0$ mol L^{-1}, 100 MPa, and 25 °C) for acid ionization of the protonated pendant arm in $[HLCrOH_2]$ is highly unusual for an uncharged carboxylic acid in water, as this quantity is invariably quite strongly negative for other such acids.[24,25] This observation vindicates the recent report by Yoshitani[19] (which appeared after this work was completed) in which a value of $\Delta V_a = +2.2 \pm 0.2$ cm^3 mol^{-1} at 0.1 MPa and infinite dilution was obtained from solution density measurements for the ionization of aqueous $[HLCrOH_2]$. As Yoshitani[19] has remarked, this surprising result is readily understood if the conjugate base $[LCrOH_2]^-$ is in labile equilibrium with a major proportion of a deaquated species $[LCr]^-$, in which L is sexidentate; the reaction volume is then anomalously positive because a molecule of coordinated water is expelled following formation of the conjugate base. This creation of a large anion reservoir will favor acid ionization, and so K_a itself is remarkably high (1.7×10^{-2} mol L^{-1}) for a carboxylic acid. This conclusion is in accord with interpretations of ^{2}H-NMR,[16] circular dichroism,[17] and Raman[18] spectra of solutions of the Cr^{III} edta complex over wide ranges of pH. The inferred quinque−sexidentate equilibrium is evidently very labile, the interconversion being rapid on the ^{2}H-NMR time scale.[16,18]

Table 3. Kinetic Parameters Defined in Equations 1, 11, and 12

parameter	value at 25.0 °C, $I = 1.0$ mol L^{-1}
k_1^0	13.4 ± 0.5 L mol^{-1} s^{-1} [a]
k_2^0	0.97 ± 0.05 L mol^{-1} s^{-1} [a]
$k_{-1}'^0$ (= $k_{-1}^0K_a^{CrNCS}$)	(1.18 ± 0.09) × 10^{-2} mol L^{-1} s^{-1} [a]
k_{-2}^0	(4.0 ± 0.6) × 10^{-2} s^{-1} [a]
K_a^0	(1.77 ± 0.05) × 10^{-2} mol L^{-1} [a]
$K_2^0 = k_2/k_{-2}$	24 ± 4 L mol^{-1} [a]
$\Delta V_1^{\ddagger}$	−13.6 ± 0.6 cm^3 mol^{-1} [b]
$\Delta V_2^{\ddagger}$	−7.8 ± 0.9 cm^3 mol^{-1} [b]
$\Delta V_{-1}'^{\ddagger}$ (= $\Delta V_{-1}^{\ddagger} + \Delta V_a^{CrNCS}$)	−13.1 ± 1.3 cm^3 mol^{-1} [b]
$\Delta V_{-2}^{\ddagger}$	9.5 ± 2.5 cm^3 mol^{-1} [b]
ΔV_a	+5.1 ± 0.6 cm^3 mol^{-1} [b]
$\Delta V_2 = \Delta V_2^{\ddagger} - \Delta V_{-2}^{\ddagger}$	+1.7 ± 2.7 cm^3 mol^{-1} [b]

[a] At 0.1 MPa. [b] At 100 MPa (mean value over experimental pressure range).

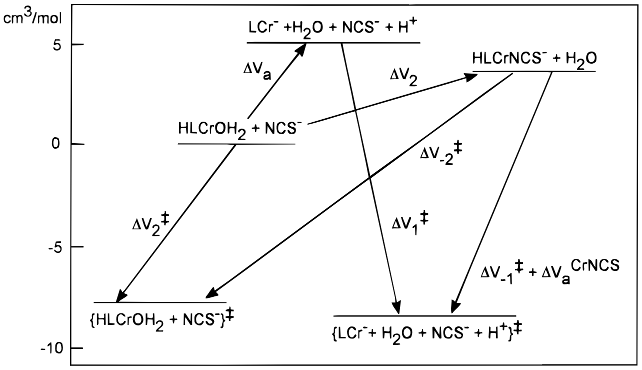

Figure 2. Molar volumes (relative to $[HLCrOH_2] + NCS^-$) of reactants, products, and transition states in the reaction of Cr^{III}(edta) species with NCS^- in acidic aqueous solution at 25.0 °C, midrange pressure (100 MPa), and $I = 1.0$ mol L^{-1} ($HClO_4/NaClO_4$).

Accordingly, in Figure 2—a diagrammatic summary of the volume data—"$[LCrOH_2]^-$" is replaced by $LCr^- + H_2O$. In Figure 2, volumes of equilibrium assemblages and transition states are given relative to that of $[HLCrOH_2] + NCS^-$, and all the participant species are included in some form at each stage to maintain a global material balance, whether or not they are involved in particular steps (e.g., ΔV_a is independent of NCS^-). Calculation of ΔV_2 as ($\Delta V_2^{\ddagger} - \Delta V_{-2}^{\ddagger}$) gives a rather uncertain result (+1.7 ± 2.7 cm^3 mol^{-1}) which is smaller than that obtained from $\Delta V_a + \Delta V_1^{\ddagger} - (\Delta V_{-1}^{\ddagger} + \Delta V_a^{CrNCS}) = +4.6 \pm 1.6$ cm^3 mol^{-1}; the value adopted for ΔV_2 in Figure 2 is therefore +3.5 ± 2.0 cm^3 mol^{-1}, the weighted mean of these values. The

---

(24) (a) Asano, T.; le Noble, W. J. *Chem. Rev.* **1978**, *78*, 407. (b) van Eldik, R.; Asano, T.; le Noble, W. *Chem. Rev.* **1989**, *89*, 549.

(25) Hamann, S. D. *Div. Appl. Chem. Tech. Pap.* (*Aust., C.S.I.R.O.*) **1972**, No. 3.

essential point is that the equilibrium volume change ΔV_2 for the reaction of [HLCrOH$_2$] with NCS$^-$ is a small, positive number.

In sharp contrast, the volumes of *activation* $\Delta V_2^{\ddagger}$ and $\Delta V_{-2}^{\ddagger}$ for the corresponding forward and reverse reactions are both markedly *negative* (Table 3 and Figure 2). This immediately rules out any simple dissociatively activated mechanism, such as has been proposed for substitution in Cr^{III} porphyrins,[1b,2−4] and is also difficult to reconcile with any externally activated associative process (I$_a$ or A), since both $\Delta V_2^{\ddagger}$ and $\Delta V_{-2}^{\ddagger}$ are numerically much larger than the volume change for the overall substitution process. The markedly negative $\Delta V_2^{\ddagger}$ and $\Delta V_{-2}^{\ddagger}$, however, and also $\Delta V_1^{\ddagger}$ and $\Delta V_{-1}'^{\,\ddagger}$ (we may assume that the ΔV_a^{CrNCS} component of $\Delta V_{-1}'^{\,\ddagger}$ is not numerically large), are at least qualitatively consistent with a common internal activating process involving transient complexation of carboxyl function on the pendant arm of the coordinated edta to the Cr center, weakening the bond of the leaving group to Cr in a seven-coordinate intermediate or possibly expelling it altogether (although the markedly negative volumes of activation suggest the former). Net reaction is observable when the arm breaks free again and the incoming ligand binds to Cr.

Such a transient chelation mechanism for substitution in Cr^{III} edta complexes was first proposed by Ogino et al.,[9] who showed that the substitutional lability of Cr^{III} complexes with ligands related to edta is greatly reduced when the pendant arm is poorly coordinating or absent. The strong evidence noted above for a labile quinque−sexidentate equilibrium in [LCrOH$_2^-$]/[LCr]$^-$ attests to the feasibility of this mechanism. A similar transient internal chelation process has been proposed to explain the marked *cis* activation of Cr^{III} complexes by potentially bidentate ligands such as nitrate,[26] acetate, and O-bonded sulfite,[27] and there is evidence that labilization by edta or similar multidentate ligands operates at other metal centers such as ruthenium(III).[28] Finally, we note that in [Fe^{III}(edta)OH$_2$]$^-$ [29] and [Mn(Hedta)OH$_2$]$^-$ [30] (high-spin 3d^5 complexes in which ligand-field effects are absent) in certain solids the edta ligands are sexidentate and the complexes are *seven*-coordinate, presumably because of strain that would be present in an octahedral sexidentate configuration. For Cr^{III}, ligand fields strongly favor octahedral coordination, but at least the precedent exists for possible *transient* seven-coordination at Cr^{III} starting from an initial state with quinquedentate edta.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support and for a Summer Undergraduate Student Research Award (to C.L.B.).

IC951110N

---

(26) Guastalla, G.; Swaddle, T. W. *Inorg. Chem.* **1974**, *13*, 61; *Can. J. Chem.* **1974**, *52*, 527.

(27) Choi, S. N.; Carlyle, D. W. *Inorg. Chem.* **1974**, *13*, 1818.

(28) Matsubara, T.; Creutz, C. *J. Am. Chem. Soc.* **1978**, *100*, 6255.

(29) Lind, M. D.; Hoard, J. L.; Hamor, M. J.; Hamor, T. A. *Inorg. Chem.* **1964**, *3*, 34.

(30) Richards, S.; Pedersen, B.; Silverton, J. V.; Hoard, J. L. *Inorg. Chem.* **1964**, *3*, 27.